

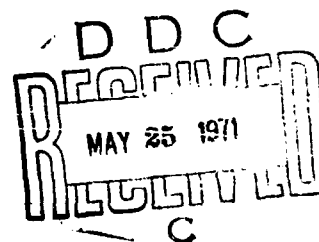
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Project NY 450 004-10
Technical Note N-326

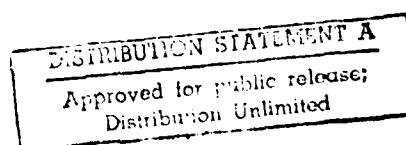
INFRARED EXAMINATION OF PROTECTIVE COATINGS

J. B. Crilly

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OBJECT OF PROJECT

To find or develop materials and techniques for arresting and/or preventing the corroding, rusting, or weathering of marine structures, shore establishment facilities, construction equipment and materials, etc., under conditions of both normal usage and storage.

OBJECT OF SUBPROJECT

To study molecular structures of organic constituents in protective coatings; to develop specification test methods to predict the behavior of protective coatings under various environments.

OBJECT OF REPORT

To present the results of tests to develop an efficient method for the identification of paint non-volatile vehicle. The requirement was to find a method that would be fast, inexpensive, and complete.

RESULTS

A method utilizing infrared spectrophotometry was developed. The time required for the identification of a typical synthetic resin is 2-1/2 hours. The cost of equipment can be met by the value of the time saved. The identification is unequivocal.

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SUMMARY

The tests showed that the identity of paint vehicle resins can be established by infrared spectrophotometry. A sample in suitable solvent was placed on a potassium bromide disk. After solvent evaporation, the sample was examined in a spectrophotometer over a chosen frequency region. The identity of the sample was established by comparison of its spectrum with spectra of samples of known constitution previously prepared. The experimental error is ± 3 percent.

INTRODUCTION

The NAVCERELAB (U. S. Naval Civil Engineering Research and Evaluation Laboratory), Port Hueneme, California, was asked by the BUDOCKS (Bureau of Yards and Docks), Washington, D. C., to study molecular structures of organic constituents in protective coatings and to develop specification test methods to predict the behavior of protective coatings under various environments, under Project number NY 450 004-10.

The specification testing of paints lacks methods for testing the nonvolatile vehicle which are as specific and exact as the tests for the pigments. Iodine number, acid number, and similar empirical values presently used are unsatisfactory detectors of adulteration or errors in compounding.

Three facts form the basis for the method of analysis to be described.

1. The infrared absorption spectrum is a unique characteristic of an organic molecule.
2. The spectrum of a mixture free of interactions, is the sum of the spectra of its constituents.
3. Samples from a mixture of constant composition will be identical within the limits imposed by experimental error.

Infrared spectrophotometry is becoming an increasingly useful tool in the quality control programs of many industrial laboratories. Its application to the examination of paint vehicles is the subject of this technical note.

EQUIPMENT

The instrument used was an infrared spectrophotometer, Beckman model IR3. It has a double monochromator and is single beamed and "memory" controlled. The high resolving power of the instrument was deliberately suppressed in order to produce a spectrum more nearly comparable to smaller, relatively inexpensive instruments which have become available recently. The sample supports were potassium bromide disks prepared in the laboratory in an evacuable die made by Applied Research Laboratories of Glendale, California. Sodium chloride disks available from Harshaw Chemical Company, Los Angeles, California, could have been used as well.

The IR3, in common with most older instruments, produces traces linear in percent transmission, $I/I_0 \times 100$, where I_0 is the amount of energy entering the sample and I is the amount leaving. Generally, however, concentration is proportional to absorbance which is the logarithm of the reciprocal of transmission. As a consequence of this, the spectrogram is inverted as to concentration, i.e., the lower the percent transmission, the higher the concentration. What appear as valleys are spoken of as peaks. A simple solution to this is to invert the spectrograms and this has been done in this report. The trace may be treated as linear in percent absorption. This is 100 minus percent transmission.

SAMPLE PREPARATION

Samples are prepared by separating pigment and vehicle using the appropriate method of Federal Specification TT-P-141, "Paint Varnish, Lacquer and Related Materials, Methods of Inspection, Sampling and Testing." Method 402.1 Pigment Content (Ordinary Centrifuge) has been found satisfactory. Care must be taken that the volatile solvents leave no interfering residue.

After the sample has been prepared, the technique will vary according to the requirements of the particular instrument available. That used in this laboratory on an alkyd vehicle will be described below.

The solution from the centrifuge was diluted with 2 vol (volumes) of benzene, 0.6 ml (milliliter) aliquots were placed on 6 potassium bromide disks and the solvent allowed to evaporate. The solvent was completely removed by heating in an oven at 85°C for 10 min. When cool, the disks were ready for examination in the spectrophotometer.

The layer of solution of benzene and vehicle on the potassium bromide proved to be an unstable duplex film. It was found that, after drying, one or two (sometimes more) of the disks appeared to have holes in them. The "hole" was, in fact, an extremely thin film of vehicle. Those disks with "holes" were rejected. The spectra of the others were recorded.

Figure 1 shows the spectrum between 5.6 and 10 μ (microns) of a typical alkyd resin based vehicle. This was the region of interest for this material.

ANALYSIS OF THE DATA

The base line technique described in American Society for

Testing Materials designation D1017-51 was modified for graphic solution. The lines were drawn through the absorption minima adjacent to the peak measured. They approximate the background absorption due to band overlap, and reflection losses.

When base lines have been drawn as shown in figure 1, two samples may be compared by superposing their base lines at the point of maximum absorption and observing spectral differences. This will give a very quick estimate of their identity or non-identity.

The question as to general type of vehicle, i.e., alkyd (figure 1), phenolic (figure 2), vinyl (figure 3), or some other such as rosin modified alkyd (figure 4), and linseed oil (figure 5), or epoxy resin (figure 6), is easily answered by inspection and comparison with spectrograms of known materials. This requires only that a library of spectra be available. The bibliography includes several references to spectra of pure compounds. Since no complete Atlas of the infrared spectra of specification paint vehicles is available, the preparation of one is under consideration. Spectra prepared in the course of the work reported here are included. The several alkyd resins are readily identified by noting the variations at the points marked by arrows.

DISCUSSION

Methodology

A large proportion of the difficulties in quantitative infrared spectrophotometry lies in the handling of small amounts of dilute solutions. Special care must be taken to keep impurities out and to deliver accurately reproducible quantities of solution. Another difficulty, in this case, is the behavior at the solution-potassium bromide interface. The condition determining the spreading behavior is simple to state but difficult to control. It is:

$$S_{b/a} = - \frac{\partial F}{\partial d_{p,T}} = W_A - W_{cb}$$

$$S_{b/a} = \text{Spreading coefficient, read as spreading coefficient of b on a.}$$

$$- \frac{\partial F}{\partial d_{p,T}} = \text{rate of decrease of free energy, F, of the system with increase of area, d, of the layer of solution at constant pressure and temperature.}$$

W_A = work required to pull the solution off 1 sq cm (square centimeter) of potassium bromide.

W_{cb} = work required to rupture a bar of solution 1 sq cm in cross section.

$$W_A = \gamma_a + \gamma_b - \gamma_{a'b'}$$

γ_a = surface tension of solution

γ_b = surface tension of substrate

$\gamma_{a'b'}$ = interfacial tension of solution on substrate.

$$W_{cb} = 2\gamma_b$$

$$S_{b/a} = \gamma_a - (\gamma_b + \gamma_{a'b'}) \text{ where the primes indicate mutual saturation.}$$

Only one of these values is controllable. That is γ_a . This may be done by change of solvent. Relatively few organic liquids are available which fulfill the requirements of solvent power, stability and volatility. γ_a is a function of solution composition. This changes as the benzene evaporates and appears to become smaller. When the "hole" appears, it is an indication that γ_a is less than $\gamma_b + \gamma_{a'b'}$ so that $S_{b/a}$ becomes negative and the layer of solution breaks up into the very thin film and a thick ring around the edge of the disk. It is this behavior which is responsible for requiring the preparation of so many replicates.

The Laboratory has tried several solvents, such as pyridine, isopropyl ether, dioxane, carbon tetrachloride, chloroform, cyclohexanone and methyl ethyl ketone. None is superior to benzene. The possibilities of mixtures are being investigated. Little advantage has appeared so far. However, it has been found that those samples which do not form holes are quite uniform in thickness and may be used with considerable confidence. Higher temperature drying conditions are also being examined and appear to hold some promise.

Costs

An estimate of the cost of the method has been made. Three tests, described in Federal Specifications TT-P-141b numbers 503.2 (rosin), 514.1 (phenolic resins), and 702.1B (phthalic anhydride), typical of those required for alkyd resin vehicles are considered. A normally well equipped laboratory is assumed and no charges for standard equipment are assessed. Standard

curves and solutions are assumed available for each method. The cost of an analyst's time and the infrared instrument only are considered.

	<u>Infra Red</u>	<u>TT-P-141b</u>
Sample preparation	2-1/4 hr	2 hr
Produce spectrum	1/2	
Read spectrum	3/4	
Analysis for phthalic acid		3 (during 2 days)
Test for phenols		1
Test for rosin		<u>1/2</u>
Total	3-1/2	6-1/2
Time charge per hour (GS-9 analyst and overhead)	\$ 5.00	\$ 5.00
Cost per sample	\$ 17.50	\$ 32.50
Initial cost of instrument	\$3850	Perkin Elmer Infra- cord
Additional equipment	<u>\$ 450</u>	Applied Research Laboratory mold
Total	\$4300	
Estimated life: 10 yr (years)		
Cost per year	\$ 430	
Service and materials	<u>\$ 100</u>	
Total annual cost	\$ 530	

Assume the low figure of 100 paint samples per year; also charge total cost of instrument to this use only.

Equipment cost per sample	\$ 5.30
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	<u>IR</u>	<u>TT-P-141b</u>
Total cost per sample:		
Time	\$ 17.50	\$ 32.50
Equipment	<u>5.30</u>	
	\$ 22.80	
Savings	\$ 9.70	

At 100 samples per yr the savings are \$970. Less 4 percent, interest on cost of special equipment (approximately \$170), they are \$800. The equipment will pay for itself in less than 6 yr when used only on these three tests on paints.

This is a very low utilization ratio - 350 hr out of more than 2000 available. Obviously, there is much time available for other work.

CONCLUSIONS

A method of sampling for the production of reproducible infra-red spectra of paint vehicles has been developed. It has been shown to be fast and inexpensive. Further work must be done to test its sensitivity to molecular structure changes.

RECOMMENDATIONS

This method of sampling for production of infrared spectra should be submitted to test by all interested activities with a view to its inclusion in future specifications.

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